Selective dehydration of glucose to 5-hydroxymethylfurfural on acidic mesoporous tantalum phosphate

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A B S T R A C T

Mesoporous tantalum phosphate was prepared from tantalum tartrate and ammonium phosphate monobasic in the presence of an ionic surfactant at room temperature, and subsequent calcined at 550 °C. This solid exhibits a high specific surface area ($256 \, m^2 \, g^{-1}$) and strong acidity ($1.48 \, mmol \, NH_3 \, g^{-1}$), and it has been successfully used as solid acid catalyst in the dehydration of glucose to 5-hydroxymethylfurfural (HMF) in a biphasic water/methyl isobutyl ketone medium. By using a glucose:catalyst weight ratio of 3:1, a glucose conversion of 56.3% and a HMF yield of 32.8% were achieved at 170 °C, and after only 1 h of reaction time. The reaction is very selective towards HMF, which is the unique product detected and moreover it is preserved from ulterior hydration to levulinic acid. Fructose was never found as by-product in the reaction. The catalyst is very stable under these experimental conditions, since no leaching of phosphorus or tantalum species to the liquid phase was found. The catalytic performance of this acid solid is well maintained after three catalytic cycles. The high catalytic activity of this mesoporous solid in the dehydration of glucose could be associated to its high acidity and the presence of both Brönsted and Lewis acid sites, which are maintained in water.

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1. Introduction

Increasingly worldwide energy demand along with diminishing fossil fuel resources and concerns about CO_2 emissions, responsible of the global warming, have stimulated the research in sustainable chemicals and fuels. Biomass, one the most abundant renewable resources has been regarded as an alternative carbon source for bio-fuels and platform chemicals [1]. Carbohydrates are the most important fraction of non-edible biomass, thus one possible route to convert these carbohydrates to useful products is through the synthesis of 5-hydroxymethylfurfural (HMF). This substance is known to be a starting material in the production of biomass-derived fuels, as well as a platform molecule for non-petroleum derived chemicals [2]. Thus, one of its derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the preparation of plastics [3]. HMF can be used to produce liquid bio-fuels and a wide range of chemicals via acid catalyzed isomerization of glucose [4]. Selective hydrogenation of HMF gives a fuel additive with combustion properties similar to ethanol, but with superior diesel miscibility [5]. The reduction of

HMF can lead to products such as 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl) tetrahydrofuran, which can serve as alcohols components in the polyesters production [6,7].

The C_6 sugars, glucose and fructose, have been used as feedstocks to produce HMF; the greatest extend of success has been achieved using fructose, which can be readily dehydrated to HMF using Brönsted acid sites [8–10]. The formation of HMF is proposed to take place through the dehydration of a five-membered ring monosaccharide. Hence, fructose which contains 21.5% of furan tautomer in aqueous solution can be converted to HMF easier than glucose which contains only 1% of such tautomeric species [11]. Although glucose is more difficult to be dehydrated, it is preferred as feedstock because it is more abundant and less expensive than fructose [10].

The challenge in the conversion of glucose to HMF is to develop catalysts that can selectively isomerize glucose to fructose, whose subsequent dehydration leads to HMF. Many different reaction systems have been studied with this purpose, such as water compatible lanthanide-based Lewis acids in biphasic solvent systems [12] or in ionic liquids [13]. On the other hand, Lewis acids from different metallic salts combined with conventional Brönsted acids, such as HCl, in a biphasic reactor [14], or metal salts in non-aqueous solvents (DMSO) under microwave radiation [15], have been also studied. However, all these catalytic systems have drawbacks

associated to the high cost of ionic liquids, high energy consumption in the case of organic solvents and corrosion when mineral acids are used. For this reason, heterogeneous catalysis is more desired for industrial applications owing to the easy recovery of solid catalysts from reaction medium which makes possible their regeneration and to their low cost. Thus, the use of heterogeneous catalysis, in combination with water as solvent, in the conversion of glucose to HMF could afford a green and low cost process.

Several heterogeneous systems have already been reported in literature for the HMF production. Thus, Qi et al. have employed TiO_2 and ZrO_2 as catalysts under microwave irradiation [16], finding that zirconia, due to its basicity, promotes isomerization of glucose to fructose, giving rise to a moderate HMF yield, (10% at a reaction temperature of 200 °C, 2 wt% glucose, substrate to catalyst weight ratio of 2, after a reaction time of 5 min), whereas anatase enhances both the isomerization and dehydration to HMF [17,18], with a yield to HMF of 18.6%. Nevertheless, a higher HMF yield (ca. 48%) can be reached by using a sulfated zirconia/alumina (1/1) in dimethylsulfoxide [19], but a sulfated ZrO_2/TiO_2 prepared by Zhang at al. [20] with a Zr/Ti molar ratio of 5.5 only allowed to attain a HMF yield of 28.8%. Layered zirconium and titanium phosphates, as well as their pyrophosphates derivatives, have been also employed as catalysts in dehydration of fructose to HMF, with moderate conversion but high selectivity, owing to the reduced formation of levulinic and formic acids [21]. High conversion and selectivity towards HMF have been reached by using heteropolyacids as solid catalysts in the dehydration of fructose, in high concentration and at moderate temperatures (115 °C) [22]. Tungstated zirconia is also active in the dehydration of fructose to HMF and the yield is associated to the presence of acid sites of medium strength [23].

Phosphates and oxides of elements belonging to 5th group of the Periodic Table also exhibit acid properties. Thus, vanadyl phosphate and mesoporous tantalum phosphate have been used as catalysts in the transesterification reaction of triglycerides to obtain biodiesel [24,25]. The water molecules coordinated to these metal species have M—OH bonds highly polarized, so that a part of the surface M—OH groups act as Brönsted acid sites. Heterogeneous catalysts based on vanadyl phosphate and derivatives obtained by partially substitution of vanadyl group by trivalent transition cations lead to catalysts with moderate activity in the dehydration of fructose, but high selectivity to HMF [26]. In the same way, hydrated niobium and tantalum oxides display strong acid properties in their amorphous form, being well maintained this behaviour even at high temperatures. These oxides supported on mesoporous silicas have been employed in the biodiesel preparation [27,28]. Niobic acid, $Nb_2O_5 \cdot nH_2O$, acts as heterogeneous catalyst with water-tolerant Lewis acid sites for the conversion of glucose to HMF in water [29]. In that work, it has been demonstrated that Lewis acid sites are the main active centres in this reaction. Yang et al. [30] have used hydrated niobium pentoxide under mild conditions as an efficient route for converting glucose into HMF with a yield of 49%. Its acidity was remarkably enhanced by treatment with phosphoric acid and calcination at 300 °C [31]. These authors have employed the hydrated tantalum oxide, which is more stable than its niobium partner, for the preparation of HMF from biomass, reaching 58% of HMF yield at 160 °C when this oxide is promoted with phosphoric acid. Carniti et al. [32] have also used niobic acid as catalyst in the dehydration of fructose, finding HMF as final product, since levulinic acid was never observed as byproduct. Niobium phosphates are other family of acid catalysts for the dehydration of fructose in aqueous medium at 100 °C, and, although the conversions are moderate, they exhibit good selectivity to HMF and low trend towards polymerization processes [33].

On the other hand, the use of mesoporous catalysts present significant advantages with respect to the conventional ones, due to their high surface areas and large pore sizes which lead to a better diffusion of reactants and products [34]. With these antecedents, the goal of the present research work is the preparation of mesoporous tantalum phosphate and its application to the dehydration reaction of glucose to HMF in a biphasic medium such as water/methyl isobutyl ketone (MIBK). The influence of several experimental parameters, such as reaction temperature, reaction time, percentage of catalyst and its reutilization, has been evaluated to optimize the experimental conditions for HMF production.

2. Experimental

2.1. Synthesis of mesoporous tantalum phosphate

The mesoporous tantalum phosphate was prepared according to the method reported by Sakar et al. [35], where tantalum penta-ethoxide was used as tantalum source. This compound was transformed into the corresponding tartrate complex by reaction with tartaric acid in absolute ethanol, employing a tartaric acid/tantalum molar ratio of 3. More details of this process have been reported elsewhere [25]. The formation of the mesostructured organo-inorganic hybrid precursor was carried out by using hexadecyltrimethylammonium bromide as surfactant, which was removed by calcination at 550 °C for 6 h to form the mesoporous tantalum phosphate.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were collected on a PAN analytical XíPert Pro automated diffractometer. Powder patterns were recorded in Bragg–Brentano reflection configuration by using a Ge (1 1 1) primary monochromator (Cu $K\alpha_1$) and the XíCelerator detector with a step size of 0.017° (2θ), the XRD patterns were obtained at low angles, between 0.5° and 10° in 2θ, with an equivalent counting time of 204.8 s/degree and at high angles, between 10° and 70° in 2θ, with 29.6 s/degree.

The textural parameters were evaluated from nitrogen adsorption–desorption isotherms at −196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. The accumulated pore volumes were determined by BJH method. The total acidity of catalysts were measured by temperature-programmed desorption of ammonia (NH_3-TPD). Catalysts (80 mg) were pre-treated at atmospheric pressure by flowing helium (35 ml min^{-1}) from room temperature to 550 °C, with a heating rate of 10 °C min^{-1} and maintaining the sample at 550 °C for 1 h. Then, catalysts were cooled until 100 °C under a helium flow and ammonia was adsorbed at this temperature. The desorption of adsorbed ammonia was carried out under a helium flow of 35 ml min^{-1}, from 100 °C to 550 °C, with a heating rate of 10 °C min^{-1} and maintaining the sample at 550 °C for 15 min. The evolved ammonia was analyzed by on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD.

FT-IR spectra of adsorbed pyridine on the catalysts were recorded on a Shimadzu Fourier Transformation Instrument (FTIR-8300) using self supported wafers of the samples. The obtained discs were placed in a greaseless stopcocks vacuum cell with CaF$_2$ windows. Self-supported wafers of samples with a weight/surface ratio of about 15 mg cm^{-2} were used. The samples were evacuated at room temperature and 10^{-2} Pa during 3 h, exposed to pyridine vapours at room temperature for 15 min and then outgassed at different temperatures.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al K_α radiation (300 W, 15 kV and 1486.6 eV) with a multi-channel detector. Spectra of samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s

at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. All recorded spectra were always fitted using Gaussian–Lorentzian curves to more accurately determine the binding energy of the different element core levels.

2.3. Catalytic test

A two-phase reactor system, consisting in water-MIBK, was employed, owing to HMF is catalytic unstable in aqueous solution. Thus, MIBK was introduced to promote the dehydration reaction by shifting the equilibrium towards its formation by extracting the HMF immediately by stirring. In this way, HMF degradation by means of processes such as fragmentation, condensation, rehydration, and ulterior dehydration reactions is avoided. Therefore, MIBK could extract more HMF with good partitioning of MHF compared to other solvents [9]. The batch bi-phase catalytic system was performed in a glass reactor of 15 mL provided with a screw top of Teflon, at 170 °C and 1 h of reaction time. Zero time was taken when temperature reached 170 °C, the stirring rate was 600 rpm. The catalytic reaction was carried out using 50 mg of solid catalyst, 0.15 g of glucose in deionized water (1.5 g) and 3.5 ml of MIBK. After reaction time, the reaction was quenched by submerging the reactor in a water bath cooled with ice; the liquid phases were separated and filtered and the analysis of products was performed in both phases. Glucose conversion and the product selectivity were calculated according to the following equations:

Glucose conversion(wt%)

$$= \frac{(\text{Mass of starting glucose} - \text{mass of remaining glucose}) \times 100}{\text{Mass of starting glucose}}$$

$$\text{Product selectivity(mol\%)} = \frac{\text{Moles of produced product} \times 100}{\text{Moles of glucose reacted}}$$

The aqueous and the organic layers were analyzed by high performance liquid chromatography (HPLC), by using a JASCO liquid chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055), column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5 μm) and PHENOMENEX REZEX RHM-Monosaccharide H+ (8%) C18 (300 mm × 7.8 mm, 5 μm). The disappearance of glucose was monitored using a refractive index detector while HMF production was monitored using a UV detector. Glucose conversion and HMF selectivity were calculated using the volumes of aqueous and organic phases used in the reaction. The solvents were filtered through a 0.45 μm filter and degassed with helium prior use. Methanol (flow rate 0.5 mL min^{-1}) and water acidified with H$_2$SO$_4$ (0.005 N) (flow rate 0.4 mL min^{-1}) were used as mobile phases in LUNA C18 and REZEX RHM columns, respectively. Injection volumes were of 6 μL, and the columns temperature was held constant at 80 °C. All samples were dissolved in methanol (LUNA C18) or water (REZEX RHM)

3. Results and discussion

3.1. Characterization of mesoporous tantalum phosphate

The full characterization of the mesoporous tantalum phosphate was already reported in a previous paper [25], and consequently its most relevant properties will be summarized. The chemical composition was determined from TG analysis, after calcination of the tantalum phosphate precursor at 550 °C and equilibrium with an atmosphere of 55% humidity. This solid retains 4.7 wt% of humidity, moreover the weight loss between 150 °C and 600 °C, which
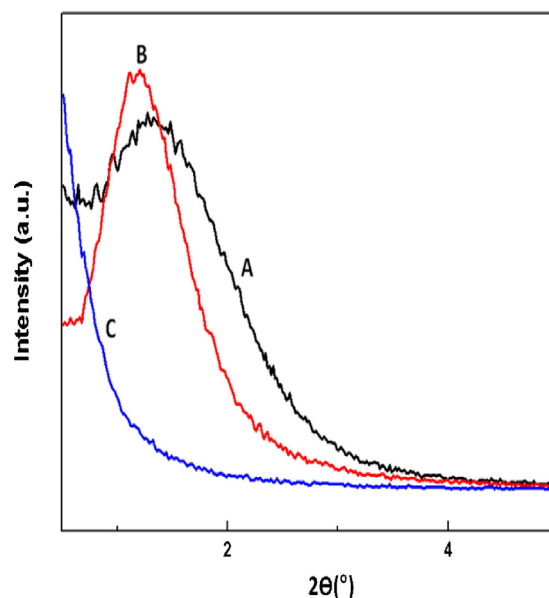
Fig. 1. XRD patterns in low angles region of mesoporous tantalum phosphate calcined at different temperatures: (A) 550 °C, (B) 750 °C and (C) 900 °C.
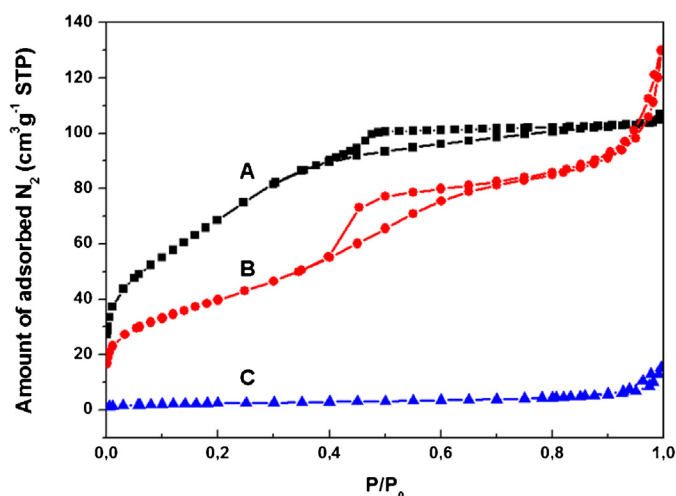
is assigned to the loss of coordinated water, thus leading to the formula: TaOPO$_4$·0.30H$_2$O, which was also corroborated by data obtained from XPS. This last technique has demonstrated that tantalum is exclusively as Ta(V). This formula reveals that not all the tantalum atoms are able to coordinate a water molecule, possibly due to the fact that they are interacting with other Ta=O groups forming the walls of the mesoporous structure, as occurs in the tetragonal anhydrous TaOPO$_4$ [36]. The existence of a mesoporous structure was confirmed by XRD at low diffraction angles, by the appearance of an intense peak at $2\theta = 1.3°$ (Fig. 1). After calcination at 750 °C this peak is still observed, revealing the high thermal stability of the mesoporous structure; but at 900 °C this peak disappears owing to the structural collapse. The coordinated water molecules are responsible for the acidity of this mesoporous phosphate, which are partially retained after evacuation at 375 °C, as inferred from the IR spectrum. By this technique, the presence of some P—OH groups is also detected at 1250 cm^{-1} [37].

The textural parameters of this tantalum phosphate and after thermal treatment at 750 and 900 °C, were evaluated from nitrogen adsorption–desorption isotherms at −196 °C. Materials calcined at 550 °C and 750 °C exhibit reversible isotherms of type IV in the IUPAC classification, with a sharp inflexion at $P/P_o = 0.35–0.45$, characteristic of capillary condensation within uniform mesopores with constant cross section (Fig. 2); moreover, the isotherms present a clear hysteresis loop. The surface areas and pore volumes decrease after the thermal treatment at 750 °C, due to the reorganization and shrinkage of the mesopore structure (Table 1). The low surface area after calcination at 900 °C confirms the structural collapse, as detected by XRD. The total acidity was determined by NH$_3$-TPD. The mesoporous tantalum phosphate has a very high acidity, 1480 μmol NH$_3$ g^{-1}, which leads to the following formula: TaOPO$_4$·0.43 NH$_3$. Since this formula contains more ammonia than water molecules (0.30 mol/mol phosphate), it indicates the presence of some Lewis acid sites and confirmed the existence of some P—OH groups; about a 33% of these acid sites are strong. The adsorption of pyridine coupled to FT-IR studies confirmed that the most abundant acid sites are Brönsted type associated to coordinated water molecules, together with some Lewis acid centres (Table 2). Almost a third of Brönsted acid sites are retained even after evacuation at 300 °C, thus revealing as strong acid sites.

Table 1
Textural parameters and acidity of mesoporous tantalum phosphate.

| Sample	S_{BET} ($m^2\,g^{-1}$)	V_p ($mL\,g^{-1}$)	Average pore diameter (d_p)	Total acidity ($\mu mol\,NH_3\,g^{-1}$)	Strong acidity (300–550 °C) ($\mu mol\,NH_3\,g^{-1}$)
TaOPO$_4$-550	255.7	0.18	2.8	1480	487
TaOPO$_4$-750	146.0	0.20	5.5	989	169
TaOPO$_4$-900	8.3	0.02	–	371	286

Fig. 2. Adsorption–desorption nitrogen isotherms at −196 °C of mesoporous tantalum phosphate activated at different temperatures: (A) 550 °C, (B) 750 °C and (C) 900 °C.

Fig. 3. Influence of the reaction medium on the dehydration of glucose. Reaction conditions: mass of catalyst = 50 mg, temperature reaction = 170 °C, 2 h of reaction time.

3.2. Catalytic study

Mesoporous tantalum phosphate has been evaluated as acid catalyst in the reaction of dehydration of glucose to HMF. As a first step, the influence of the nature of the reaction medium on the conversion, as well as on the selectivity to HMF, was studied. Three different media were considered: water, water/methyl isobutyl ether and water/MIBK. The obtained results, at 160 °C and 2 h of reaction time, are gathered in Fig. 3, and reveal that the conversion and the selectivity depend on the presence of the organic phase where the extraction of HMF takes place [9]. The aqueous system is the most effective with the higher conversion (63.9%) but exhibiting the lower selectivity and yield of HMF. In contrast, the system formed by water/MIBK is the most efficient (25.5% of HMF yield) owing to the high value for the HMF partition coefficient in MIBK/water (1.1). The biphasic methyl-isobutylether/water presents an intermediate behaviour with a partition coefficient for HMF of only 0.23. Therefore, the yield of HMF can be improved by using a biphasic system, where the organic phase is able to extract the HMF formed in the aqueous medium, thus increasing the selectivity towards HMF. It is well known that the selectivity in an aqueous medium is lower as a consequence of the fact that equilibrium is not shifted towards the HMF formation and the low stability of HMF in this medium where suffers condensation reactions [9] or acetalization with glucose [38], thus reducing considerably the HMF yield.

Table 2
Concentration of Brönsted (C_B) and Lewis (C_L) acid sites at room temperature, as determined by FT-IR spectroscopy of adsorbed pyridine, after thermal treatment of TaOPO$_4$ at different temperatures.

Temperature (°C)	C_B ($\mu mol\,g^{-1}$)	C_L
25	288	36
250	309	97
375	290	50
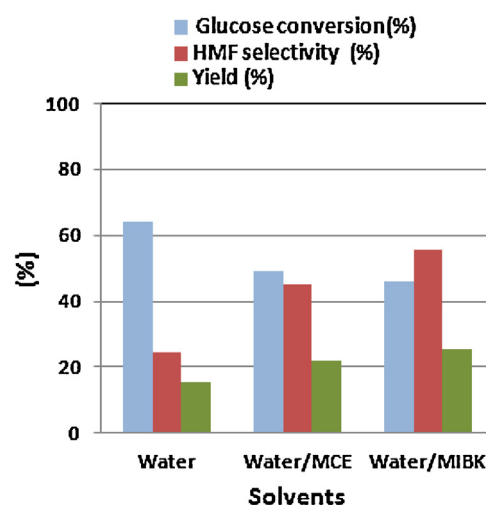
Secondly, the influence of the temperature on the catalytic reaction has been explored, employing as reaction medium the biphasic water/MIBK, and 2 h of reaction time. The catalytic results reflect that glucose conversion rises with temperature, achieving a value of 93.7% at 180 °C, but HMF selectivity shows an opposite trend (Fig. 4). Accordingly, at 170 °C, good conversion and selectivity were obtained with 37.8 mol% of HMF yield. For this reason, this temperature was selected as reaction temperature to study other parameters influencing on this catalytic reaction. In this reaction, only HMF was detected as reaction product. Fructose was never found and, assuming that the isomerization of glucose to fructose occurs in alkaline medium or in the presence of basic sites, this fact would point to that mesoporous tantalum phosphate, as expected,
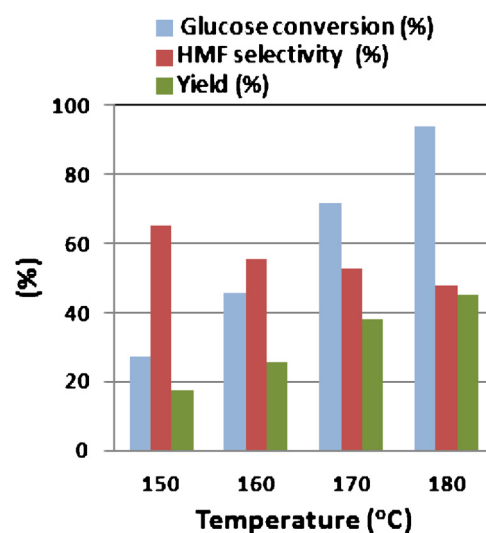
Fig. 4. Effect of temperature on the dehydration of glucose on mesoporous tantalum phosphate: reaction time = 2 h, mass of catalyst = 50 mg.

lacks of such type of active sites. On the other hand, when glucose is treated at 170 °C during 2 h under these experimental conditions, but without catalyst, no transformation into fructose and/or HMF was detected. This behaviour is different to that reported by Watanabe et al. [18] which, in hot compressed water at 200 °C, detected the formation of fructose and HMF from glucose. All these data lead to think that, employing mesoporous tantalum phosphate as catalyst in the dehydration of glucose, the formation of HMF does not involve the isomerization to fructose; on the contrary, this compound is formed from ring-opening intermediates derived from glucose in the presence of the catalyst, which are very unstable [39]. Nevertheless, the isomerization to fructose and its fast transformation into HMF can also take place [18] owing to the presence of water tolerant Lewis acid sites on the catalyst surface (Table 2) [29]. These Lewis acid sites enable to produce the dehydration of glucose, even after the formation of the corresponding water adducts in this medium, owing to the high capability of glucose for complexes formation. To check the participation of Lewis acid sites in this reaction, the mesoporous tantalum phosphate has been treated with excess of KOH during 1 h and later rinsed with water till neutral pH, in order to neutralize the Brönsted acid sites. The resulting catalyst was assayed under similar experimental conditions, leading to 33.8% of glucose conversion and 29.7% of HMF selectivity, which is expected to be exclusively attributed to the activity of the Lewis acid sites. Recently, it has been reported the synergism between a protonated phosphate group and a nearby metal Lewis centre in a niobium phosphate catalyst, which could produce the dehydration of glucose to HMF in a two-stage process. In a first step, the isomerization of glucose to fructose occurs over Lewis acid sites and then the subsequent dehydration of fructose to HMF over protonated phosphate groups, without intermediate desorption of fructose molecules, takes place [40]. A similar mechanism could also be proposed for the case of the mesoporous tantalum phosphate. Therefore, it can be concluded that the dehydration of glucose into HMF over the pristine mesoporous tantalum phosphate occurs with the participation of both Brönsted and Lewis acid sites. The high catalytic activity observed in the present work is not surprising, since this acid solid catalyst exhibits both Brönsted and Lewis acid sites, with a total acidity of 1480 μmol NH$_3$ g^{-1}, being strong as deduced from pyridine adsorption coupled to FT-IR spectroscopy (Table 2).

On the other hand, it is noteworthy that mesoporous tantalum phosphate shows a high selectivity towards HMF and, at the same time, the rehydration of HMF to produce levulinic acid is unfavoured. This finding is in contrast with that reported for homogeneous and heterogeneous catalysts based on ion exchange resins [41]. The formation of levulinic acid was found as a consequence of the presence of high strength acid sites and for larger reaction times [42]. That means that mesoporous tantalum phosphate, in spite of possessing strong acid sites, its strength is not enough to produce this transformation. To verify this assumption, the catalyst was put in contact with HMF under similar experimental conditions (170 °C, 2 h) in the same biphasic system. After this time, levulinic acid was not detected, thus corroborating that mesoporous tantalum phosphate is unable to rehydrate HMF. Moreover, all HMF could be recovered without transformation in other substances, such as soluble polymers or humins; this fact reveals that in this case these substances do not proceed directly from HMF but from the intermediates between glucose and HMF, as was reported by Kuster et al. [43] in the case of fructose. On the other hand, it can be also deduced from Fig. 4 that, as expected, the selectivity decreases with the reaction temperature. This is due to that, although conversion rises with temperature, the formation of intermediate species is favoured, leading to more soluble polymers and humins. After some minutes of reaction, the catalyst change of colour from white to brown, due to deposition of residues and polymers formed from
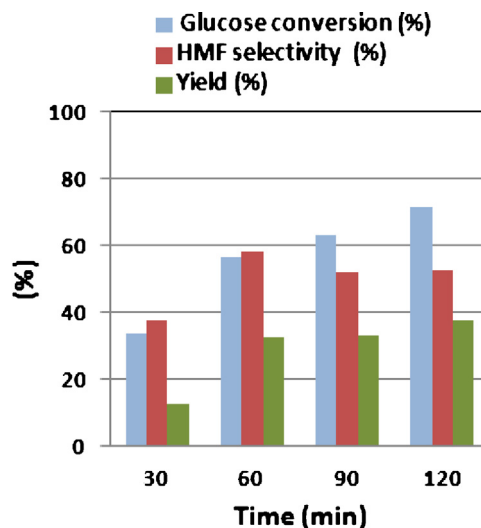

Fig. 5. Dependence of the reaction time on the dehydration reaction of glucose. Reaction conditions: temperature = 170 °C, mass of catalysts = 50 mg.

saccharides in the presence of an acidic catalyst [44,45]. The presence of these residues on the catalyst surface is responsible for the lowering of the glucose conversion and HMF selectivity.

The comparison of the results found in the present work with those reported in literature and obtained with other heterogeneous catalysts is difficult owing to the different experimental conditions used in each case. Furthermore, the number of works devoted to study the dehydration of glucose in water is quite scarce. Thus, the HMF yield obtained with this mesoporous tantalum phosphate is higher than those found when titania or zirconia are employed as catalysts in water at 200 °C or in hot compressed water, even with microwave heating [16–18]. On the other hand, the results obtained in the present work are better than those reported with niobium phosphate at 135 °C, where a low HMF yield is achieved [40]. Only better results are obtained when niobic acid was treated with phosphoric acid 1 M, although the HMF yield was close to 40% [30].

Once the temperature of reaction was chosen, the reaction time was studied (Fig. 5). The data demonstrate that the reaction is quite fast, since after 30 min an important conversion was achieved. For times higher than 1 h the conversion increases only monotonously, possible due to the deposition on the surface of the catalyst of residues formed from intermediates condensation in water which mask some active sites. At the same time, the maximum selectivity is achieved after 1 h, decreasing then due to the formation of soluble polymers and humins. By using mesoporous tantalum phosphate, the conversion of glucose into HMF is faster than with hydrated niobium oxide treated with phosphoric acid [30]. Possibly, the mesoporous network facilitates the rapid diffusion of reactants and products and, achieving a TOF of 63 mmol of HMF g$_{cat}$$^{-1}$ h^{-1}; this value is 3.5 times higher than that found in the case of hydrated niobium oxide. For this reason, this catalyst could be useful for large scale and sustainable preparation of HMF from glucose as raw material. From these data, 1 h of reaction time was selected to optimize the rest of parameters of the catalytic process.

Since the catalyst concentration affects the glucose conversion, the influence of the amount of catalyst (50–100 mg) has been also evaluated. Fig. 6 shows that the conversion increases monotonously with the weight of catalyst, but the selectivity that initially also increases with this experimental parameter, beyond 50 mg of catalyst a decrease is observed; this could be a consequence of the formation of a higher amount of condensation products from the intermediates of glucose or glucose acetalization with HMF in the
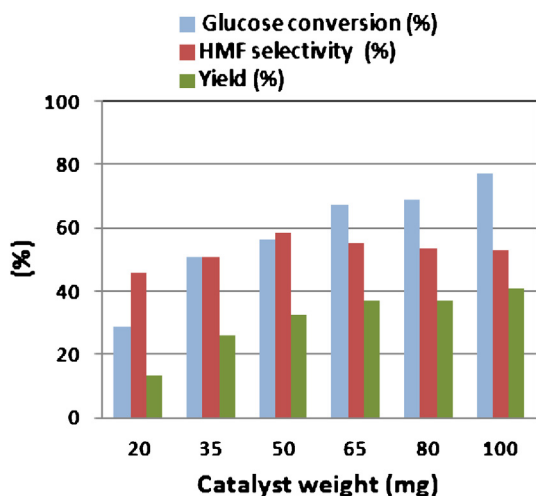
Fig. 6. Trend of the conversion of glucose, selectivity and yield of HMF as a function of the loading of catalyst. Reaction conditions: temperature = 170 °C, reaction time = 1 h.

aqueous medium. The almost lineal increment of conversion with the catalyst weight means that there is not diffusional limitation in the glucose dehydration process.

Heterogeneous acid catalysts take advantages of the easy recovering from the reaction medium against liquid acids, and thus they can be reused as such or after regeneration. In the present study, the spent catalyst after 1 h of reaction was reused, without any pretreatment, washing or thermal treatment, in new catalytic cycles. Fig. 7 shows the results of four successive reactions, where it can be observed that the catalytic activity is well maintained, especially in the former three cycles with HMF yields above 22.3%. The small loss of activity with respect to the first reaction cycle could be due to the acid site blockage by some adsorbed intermediates or humins. However, after these three cycles of reaction the catalyst was separated by filtration, rinsed with hexane and calcined at 550 °C during 2 h. Then the catalyst was again tested under the same experimental conditions and its catalytic activity was completely recovered since the HMF yield was again 32%. Simultaneously with the reutilization test, it was evaluated the possible leaching of tantalum or phosphate ions into the reaction medium. For this purpose, the catalyst was separated by filtration and the resulting liquid was analyzed by ICP to determine the presence of both species. The analytical results reveal that the concentration of both species in the aqueous
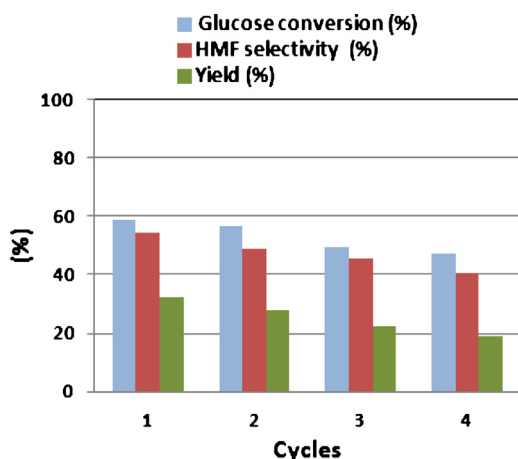
phase is 0.06 ppm of phosphorus and 0.33 ppm of tantalum, thus indicating the great stability of the catalyst under the experimental conditions.

In summary, mesoporous tantalum phosphate functions as a heterogeneous catalyst for the dehydration of glucose to HMF in a bi-phasic water/MIBK medium, with high selectivity and the absence of side-reactions, since levulinic or formic acids were not found in any case. The selective transformation of glucose into HMF, the most important intermediate between bio-chemicals and petroleum based-chemicals, by using this mesoporous acid solid makes the process of glucose conversion into HMF environment-friendly and cost effective. Its suitable catalytic activity could be correlated with the mesoporous structure, intrinsic acidity and the presence of both types of acid sites (Lewis and Brönsted), which are maintained in water.

Acknowledgements

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Fig. 7. Reusability test of the catalyst in the dehydration reaction of glucose. Reaction conditions: mass of catalyst = 50 mg, temperature = 170 °C, reaction time = 1 h.

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